

# IMPOSSIBILITY OF THE EXISTENCE OF THE UNIVERSAL DENSITY FUNCTIONAL

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Using the virial theorem, it is shown that the hypothesis of the existence of the universal density functional is invalid.

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The density functional theory (DFT) is based on two statements formulated in the known paper by Hohenberg and Kohn [1]. According to the first statement conventionally referred to as the Hohenberg-Kohn theorem, the ground state energy of the inhomogeneous electron gas in a static external field is the functional of the inhomogeneous electron density. The Hohenberg-Kohn theorem proof is based on the lemma [1,2]: the inhomogeneous density  $n(\mathbf{r})$  in the ground state of a bound system of interacting electrons in a certain static external field characterized by the potential  $\varphi^{ext}(\mathbf{r})$  uniquely defines this potential. In this case, according to [1,2]: (i) here the term "uniquely" means "with an accuracy" to an additive constant of no interest; (ii) in the case of a degenerate ground state, the lemma relates to the density  $n(\mathbf{r})$  of any ground state. The requirement of the ground state non-degeneracy is easily eliminated [3]; (iii) the lemma is mathematically rigorous.

According to the lemma, the inhomogeneous density  $n(\mathbf{r})$  corresponding to the ground state and the external field potential  $\varphi^{ext}(\mathbf{r})$  are biunique functionals,

$$\varphi^{ext}(\mathbf{r}) = \varphi^{ext}(\{n(\mathbf{r})\}) \leftrightarrow n(\mathbf{r}) = n(\{\varphi(\mathbf{r})\}), \quad (1)$$

Thus, for the ground state energy  $E_0$  of the system of interacting electrons with Hamiltonian  $H$  in an external field with potential  $\varphi^{ext}(\mathbf{r})$ , characterized by the wave function  $|\Psi_0\rangle$ , we can write

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = E_0(N, \{\varphi(\mathbf{r})\}) = E_0(\{n(\mathbf{r})\}), \quad (2)$$

Let us pay attention that the lemma is a direct consequence of the Rayleigh-Ritz minimum principle which, as applied to quantum mechanics, is written as (see, e.g., [4,5])

$$E_0 \leq \langle \Psi | H | \Psi \rangle, \quad \langle \Psi | \Psi \rangle = 1 \quad (3)$$

where  $|\Psi\rangle$  is any normalized wave function for the system of  $N$  electrons. In non-strict inequality (3), equality takes place only in the case when  $|\Psi\rangle = |\Psi_0\rangle$ . However, direct application of variational inequality (3) to the DFT is impossible, since this inequality implies variation of the wave function  $|\Psi\rangle$ , rather than the density  $n(\mathbf{r})$ . The point is that, according to the Hohenberg-Kohn theorem, only the ground state energy is a density functional. To obtain a variational inequality similar to (3), but implying the possibility of varying the inhomogeneous density, Hohenberg and Kohn [1] formulated the second statement that the quantity  $\langle \Psi_0 | T + U | \Psi_0 \rangle$  is a universal functional of density  $n(\mathbf{r})$ ,

$$F^{univ}(\{n(\mathbf{r})\}) = \langle \Psi_0 | T + U | \Psi_0 \rangle = E_0(\{n(\mathbf{r})\}) - \int \varphi^{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (4)$$

where  $T$  and  $U$  are the operators of the kinetic energy and interparticle interaction energy of electrons, respectively. In this case, the universality is understood as the functional independence of the form and value of the external field  $\varphi^{ext}(\mathbf{r})$ . In contrast to the Hohenberg-Kohn theorem, the second statement (4) is accepted in the DFT without proof. Moreover, the exact form of this universal functional is still unknown even for noninteracting particles ( $U = 0$ ). However, the use of the assumption on the existence of such a universal functional makes it possible to "create" a variational procedure for determining the inhomogeneous density  $n(\mathbf{r})$  corresponding to the ground state of the system under consideration. The essence of this procedure is reduced to the following: let the explicit form of the

density functional for ground state energy  $E_0(\{n(\mathbf{r})\})$  be a priori known, whereas the inhomogeneous density  $n(\mathbf{r})$  corresponding to the ground state is unknown. Then, to determine  $n(\mathbf{r})$ , according to (4), the inequality [1,2]

$$E_0(\{n(\mathbf{r})\}) \leq E_0(\{\tilde{n}(\mathbf{r})\}) \quad (5)$$

should be used, where  $\tilde{n}(\mathbf{r})$  is any positive function satisfying the condition  $\int \tilde{n}(\mathbf{r}) d\mathbf{r} = 1$ . In this case, equality in (5) takes place if  $\tilde{n}(\mathbf{r}) = n(\mathbf{r})$ . Thus, the DFT loses practical meaning without statement (4), since the use of only the Hohenberg-Kohn theorem does not "relieve the need" to find a many-body wave function to determine the inhomogeneous density.

Let us now show that statement (4) is invalid. We perform the proof "to the contrary" by analogy with the proof of the lemma [1,2]. Indeed, if the functional  $F^{univ}(\{n(\mathbf{r})\})$  is a universal functional of the inhomogeneous density  $n(\mathbf{r})$ , its variational derivative with respect to the density is also a universal functional,

$$G^{univ}(\{n(\mathbf{r})\}) = \frac{\delta F^{univ}(\{n(\mathbf{r})\})}{\delta n(\mathbf{r})} \quad (6)$$

Substituting the last equality on the right-hand side (4) into (6), and taking into account that  $\langle \delta \Psi_0 | H | \Psi_0 \rangle + \langle \Psi_0 | H | \delta \Psi_0 \rangle = 0$  we find

$$G^{univ}(\{n(\mathbf{r})\}) = \frac{\delta E_0(\{n(\mathbf{r})\})}{\delta n(\mathbf{r})} - \varphi^{ext}(\{n(\mathbf{r})\}) - \int n(\mathbf{r}_1) \frac{\delta \varphi^{ext}(\{n(\mathbf{r}_1)\})}{\delta n(\mathbf{r})} d\mathbf{r}_1 \quad (7)$$

Taking into account (1) and (2) one arrive at

$$\frac{\delta E_0(\{n(\mathbf{r})\})}{\delta n(\mathbf{r})} = \int \frac{\delta E_0(N, \{\varphi^{ext}(\mathbf{r})\})}{\delta \varphi^{ext}(\mathbf{r}_1)} \frac{\delta \varphi^{ext}(\mathbf{r}_1)}{\delta n(\mathbf{r})} d\mathbf{r}_1, \quad \frac{\delta E_0(N, \{\varphi^{ext}(\mathbf{r})\})}{\delta \varphi^{ext}(\mathbf{r})} = n(\mathbf{r}) \quad (8)$$

It follows from (7) and (8) that

$$G^{univ}(\{n(\mathbf{r})\}) = -\varphi^{ext}(\{n(\mathbf{r})\}) \quad (9)$$

Thus, if the quantity  $F^{univ}(\{n(\mathbf{r})\})$  is a universal density functional, the external field potential is also a universal functional of the inhomogeneous density. Furthermore, according to (4), the ground state energy  $E_0$  is also a universal functional of the inhomogeneous density. These statements are easily refuted using the virial theorem. Indeed, in the case of finite motion of the system of noninteracting ( $U = 0$ ) particles in the external field  $\varphi^{ext}(\mathbf{r})$ , according to the virial theorem (see [6] and references therein), we have

$$2\langle \Psi_0 | T | \Psi_0 \rangle - \int n(\mathbf{r}) (\mathbf{r} \cdot \nabla \varphi^{ext}(\mathbf{r})) d\mathbf{r} = 0 \quad (10)$$

If a homogeneous coordinate power function  $\varphi^{ext}(\mathbf{r}) \sim r^m$  can be chosen as a particular case for the external field potential, then

$$\langle \Psi_0 | T | \Psi_0 \rangle = \frac{m}{2} \int \varphi^{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}, \quad E_0 = \left( \frac{m}{2} + 1 \right) \int \varphi^{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (11)$$

Hence, if the external field potential is a universal functional (9), both quantities in (11) are not universal density functionals (they depend on the field parameter  $m$ ), and we come to contradiction. Thus, the hypothesis of the existence of the universal density functional (4) is invalid. We note that the doubts on the possible existence of the universal density functional were probably first casted by Gilbert [7], but in this paper it was only an assumption, related solely with consideration of the nonlocal type of an external field.

Therefore, the development of the density matrix functional theory (DMFT) becomes particularly urgent (see, e.g., [8,9] and references therein). At the same time, the DMFT is consistent with the virial theorem, including the case of the consideration of the volume occupied by the system [10]. We note that on the basis of the virial theorem appears the way for introduction of the really universal DMFT.

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